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54 Mild hydrocracking with a catalyst having a narrow pore distribution.

57 Mild hydrocracking of hydrocarbon oils is accomplished with a catalyst containing nickel and molybdenum as active metals, and phosphorus, on an amorphous porous refractory oxide having a narrow pore size distribution and a small mode pore diameter.

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Mild hydrocracking with a catalyst having a narrow pore size distribution

The invention relates to a process for mild hydrocracking hydrocarbon oils. More particularly, the invention relates to a mild hydrocracking catalytic process for treating vacuum gas oils and residuum hydrocarbon feedstocks.

In the refining of hydrocarbon oils, it is often desirable to subject the hydrocarbon oil to catalytic hydroprocessing. One such process is hydrocracking, a process wherein, in the typical instance, a gas oil or residuum feedstock is passed with hydrogen through a bed of catalyst active for cracking relatively high molecular weight compounds to more desirable, relatively low molecular weight compounds of lower boiling point. In addition, because the catalyst has hydrogenation activity, the cracked products are saturated by hydrogenation while organosulfur and organonitrogen compounds in the feed are converted to hydrogen sulfide and ammonia, respectively, both of which are usually removed in gas-liquid separators. Thus, the advantage of hydrocracking lies in the conversion of a sulfur-containing and/or nitrogen-containing gas oil feed, boiling, for example, mostly above about 370°C (700°F), to a relatively sulfur and nitrogen-free product of boiling point below 370°C (700°F), such as gasoline, jet fuel, diesel fuel, and mixtures thereof.

Recently, attention has been directed to "mild hydrocracking." The cost of constructing a hydrocracking unit operating at high pressures is quite significant and poses a major economic obstacle to its use. Accordingly, interest has developed in converting existing hydroprocessing units, such as hydrotreating or hydrodesulfurization units, into hydrocracking units. It is realized, of course, that hydrotreating units and the like, especially once-through units, are not normally designed for optimum hydrocracking conditions, and specifically, for the high pressures usually employed in commercial hydrocracking, i.e., above 103 bar (1,500 p.s.i.g.). Nevertheless, there is still an advantage if even some hydrocracking can be achieved under the low pressure constraints of typical hydrotreating or hydrodesulfurization units, and the challenge to the art is to discover hydrocracking catalysts having sufficient activity and activity maintenance to be commercially useful under such mild hydrocracking conditions.

Therefore, an aim of the art is to provide a mild hydrocracking catalyst having a high activity, selectivity and stability. Activity may be determined by comparing the temperature at which various catalysts must be utilized under otherwise constant mild hydrocracking conditions with the same feedstock so as to produce a given percentage (usually between 10 and 50 volume percent) of products boiling at or below 370°C (700°F). The lower the temperature for a given catalyst, the more active such a catalyst is for mild hydrocracking. Alternatively, activity may be determined by comparing the percentages of products boiling at or below 370°C (700°F) when various catalysts are utilized under otherwise constant mild hydrocracking conditions with the same feedstock. The higher the percentage of 370°C (700°F)-minus product converted from the components in the feedstock boiling above 370°C (700°F) for a given catalyst, the more active such a catalyst is in relation to a catalyst yielding a lower percentage of 370°C (700°F) - minus product. Selectivity of a mild hydrocracking catalyst may be determined during the foregoing described activity test and is measured as that percentage fraction of the 370°C (700°F) - minus product boiling in the range of middle distillate or midbarrel products, i.e. 150°C - 370°C (300°F - 700°F). Stability is a measure of how well a catalyst maintains its activity over an extended time period when treating a given hydrocarbon feedstock under the conditions of the activity test. Stability is generally measured in terms of the change in temperature required per day to maintain a 40 volume percent or other given conversion (usually less than 50 volume percent).

The invention provides a mild hydrocracking process that uses a catalyst containing active nickel and molybdenum hydrogenation metal components and a phosphorus component supported on an amorphous porous refractory oxide wherein the catalyst has a narrow pore size distribution including at least 75 percent of the total pore volume in pores in diameter from about 50 to about 130 angstroms and less than 10 percent of the pore volume in pores of diameter greater than 110 angstroms. Preferably, the catalyst has at least about 60 percent of the pore volume in pores of diameter within about 20 angstroms above or below a mode pore diameter in the range from about 55 to about 100 angstroms. Preferably the mode pore diameter is in the range from about 60 to about 90 angstroms. In the process of the invention a hydrocarbon feedstock such as a vacuum gas hydrocarbon oil is mildly hydrocracked, with simultaneous hydrodesulfurization and hydrodenitrogenation, by contact with the catalyst under mild hydrocracking conditions correlated so as to convert from about 10 to about 50 volume percent of the feedstock fraction boiling above 370°C (700°F) to hydrocarbon products boiling at or below about 370°C (700°F). The process conditions preferably include a hydrogen partial pressure less than about 103 bar (1,500 p.s.i.g.).

Preferred amorphous porous refractory oxides are silica, alumina, silica-alumina, magnesia, silica-magnesia, zirconia, silica-zirconia, titania, silica-titania and silica-zirconia-titania.

The most preferred amorphous refractory oxide for use in the invention comprises gamma alumina or a similarly active alumina. One of the most important discoveries in the invention is that gamma alumina and related materials having a relatively small mode pore diameter and a narrow pore size distribution are useful under the relatively unfavorable conditions of mild hydrocracking of gas oils to lower boiling distillates.

5 Thus the invention provides a process as defined in the appended claims.

In preferred embodiments of the process, a catalyst containing an amorphous refractory oxide, such as alumina, has an average pore diameter from about 50 to about 110 angstroms, preferably about 55 to about 100 angstroms, and most preferably about 60 to about 90 angstroms. The catalyst has a narrow pore size distribution wherein at least about 50 percent, preferably at least about 65 percent, and more preferably at
10 least about 75 percent is in pores distributed over a narrow range of about 20 angstroms above to about 20 angstroms below the mode pore diameter as measured by mercury porosimetry.

In the preparation of the catalysts used in the present invention, the pore size distribution of the amorphous support particles may be similar to that of the final catalyst, but this is not necessary nor critical. The amorphous refractory oxide support material is typically comprised of such amorphous inorganic
15 refractory oxides as silica, magnesia, silica-magnesia, zirconia, silica-zirconia, titania, silica-titania, alumina, silica-alumina, etc., with supports containing gamma, theta, delta, and/or eta alumina being highly preferred. Preferred support particles having the preferred physical characteristics disclosed herein are commercially available from Nippon-Ketjen Catalyst Division of AKZO-Chemie, and American Cyanamid, Inc. Mixtures of the foregoing oxides are also contemplated, especially when prepared as homogeneously as possible.

20 The amorphous refractory oxide support material is usually prepared in the form of shaped particulates, with the preferred method being to extrude a precursor of the desired support through a die having openings therein of desired size and shape, after which the extruded matter is cut into extrudates of desired length. The support particles may also be prepared by mulling (or pulverizing) a precalcined amorphous refractory oxide to a particle size less than about 100 microns and extruding the material.

25 The extruded particles may have any cross-sectional shape, i.e., symmetrical or asymmetrical, but most often have a symmetrical cross-sectional shape, preferably a cylindrical or polylobal shape. The cross-sectional diameter of the particles is usually about 0.64 to about 3.2mm (about 1/40 to about 1/8 inch), preferably about 0.79 to about 2.1mm (about 1/32 to about 1/12 inch), and most preferably about 1.1 to about 1.7mm (about 1/24 to about 1/15 inch). Among the preferred catalyst configurations are cross-sectional shapes resembling that of a three-leaf clover, as shown, for example, in Figures 8 and 8A of US-A-
30 4 028 227. Preferred clover-shaped particulates are such that each "leaf" of the cross-section is defined by about a 270° arc of a circle having a diameter between about 0.51 and 1.3mm (0.02 and 0.05 inch). Other preferred particulates are those having quadra-lobal cross-sectional shapes, including asymmetrical shapes, and symmetrical shapes such as in Figure 10 of US-A-4 028 227. Other particulates are available from
35 Davison Chemical Company, a division of W. R. Grace & Company, having ring and minilith shapes, as disclosed in US-A-4 510 261.

Typical characteristics of the amorphous refractory oxide supports utilized herein are a total pore volume, mode pore diameter and surface area large enough to provide substantial space and area to deposit the active metal components. The total pore volume of the support, as measured by conventional
40 mercury porosimeter methods, is usually about 0.2 to about 2.0 cc/gram, preferably about 0.25 to about 1.0 cc/gram, and most preferably about 0.3 to about 0.9 cc/gram. Surface area (as measured by the B.E.T. method) is typically above about 100m²/gram, and preferably about 125m²/gram to about 400m²/gram. Physical characteristics of three amorphous refractory oxide supports utilized in preparation of catalyst employed in the process of the invention are summarized in Table A as follows:

TABLE A

	Pore Diameter Angstroms	Support X % Pore Volume	Support Y % Pore Volume	Support Z % Pore Volume
5	40-50	-	-	4.0%
10	<50	0.8%	-	-
	50-60	5.7%	4.0%	16.0%
	60-70	16.4%	15.0%	46.0%
15	70-80	29.9%	61.0%	28.0%
	> 80	-	-	6.0%
20	80-90	24.6%	13.0%	-
	> 90	-	7.0%	-
25	90-100	9.8%	-	-
	100-110	6.6%	-	-
	110-120	1.6%	-	-
30	120-130	0.8	-	-
	>130	5.7%	-	-
35	PORE VOLUME cc/gram (Merc. Poros.)	0.61	0.63	0.58
40	MODE PORE DIAMETER (Merc. Poros.)	~ 88	~ 76	~ 67

To prepare the mild hydrocracking catalyst, the support material is compounded, as by a single impregnation or multiple impregnations of a calcined amorphous refractory oxide support particles, with one or more precursors of at least one catalytically active hydrogenation metal component. The impregnation may be accomplished by any method known in the art, as for example, by spray impregnation wherein a solution containing the metal precursors in dissolved form is sprayed onto the support particles. Another method is the circulation or multi-dip procedure wherein the support material is repeatedly contacted with the impregnating solution with or without intermittent drying. Yet another method involves soaking the support in a large volume of the impregnation solution, and yet one more method is the pore volume or pore saturation technique wherein support particles are introduced into an impregnation solution of volume just sufficient to fill the pores of the support. On occasion, the pore saturation technique may be modified so as to utilize an impregnation solution having a volume between 10 percent less and 10 percent more than that which will just fill the pores.

If the active metal precursors are incorporated by impregnation, a subsequent or second calcination, as for example at temperatures between 400°C (750°F) and 760°C (1400°F), converts the metals to their respective oxide forms. In some cases, calcinations may follow each impregnation of individual active metals. Such multiple impregnation-calcination procedures, however, may be avoided in alternative embodi-

ments of the invention, as for example, by commulling all the active metals with the support materials rather than impregnating the metals thereon. In commulling, precursors of the support materials usually in a hydrated or gel form, are admixed with precursors of the active metal components, either in solid form or in solution, to produce a paste suitable for shaping by known methods, e.g., pelleting, extrusion, etc. A subsequent calcination yields a mild hydrocracking catalyst containing the active metals in their respective oxide forms.

When the mild hydrocracking catalyst is prepared by the foregoing or equivalent methods, at least one active metal component having hydrogenation activity, typically one or more metal components from the Group VIB and VIII metals of the Periodic Table of Elements, is introduced into the catalyst. Preferably, the catalyst contains both a Group VIB and VIII element as hydrogenation metals, with cobalt or nickel and molybdenum or tungsten being the preferred combination of active metals, and nickel and tungsten being most preferred. The catalyst contains up to about 10, usually from 1 to 8 percent, and preferably from 2 to 6 percent by weight of the Group VIII metal, calculated as the monoxide, and up to about 30, usually from about 3 to about 28 percent, and preferably from 8 to 26 percent by weight of the Group VIB metal, calculated as the trioxide. A highly preferred catalyst useful herein contains about 17 to about 27 weight percent of Group VIB metal components, calculated as the trioxide, and from about 0.5 to about 8 weight percent of Group VIII metal components, calculated as the monoxide. (Note: if molybdenum is selected as the active metal, it generally is solubilized with phosphoric acid, ammonium hydroxide, citric acid, and the like, during the preparation of the catalyst. Therefore, molybdenum-containing catalysts will often further contain a phosphorus component on the catalyst, which phosphorus component may provide acid properties to the catalyst or act as a catalytic promoter. Typically the catalyst contains about 1 to about 6 weight percent of phosphorus components, calculated as P.)

The physical characteristics of the mild hydrocracking catalyst will usually vary from those of the support particles by less than about 25 percent. Ordinarily, the mild hydrocracking catalyst is prepared so as to have a narrow pore size distribution wherein at least about 75 percent, preferably at least about 80 percent, and most preferably at least about 85 percent of the total pore volume is in pores of diameter from about 50 to about 130 angstroms. Ordinarily the catalyst has less than about 10 percent of the total pore volume in pores of diameter below about 50 angstroms and preferably less than about 0.05 cc/gram. Also, the catalyst has less than about 10 percent of the pore volume in pores of diameter greater than about 130 angstroms, preferably less than about 0.05 cc/gram.

Another porosity feature of the catalyst is the narrow pore size distribution of the pores of diameter greater than the mode pore diameter. The mode pore diameter of the catalyst usually lies in the range from about 50 to about 115 angstroms, preferably 55 to about 100 angstroms, and most preferably about 60 to about 90 angstroms. Ordinarily, at least about 40 percent of the total pore volume is in pores of diameter between the mode pore diameter and less than about 90 angstroms, preferably less than about 50 angstroms, and most preferably less than about 25 angstroms above the mode pore diameter. With respect to small pores, at least about 40 percent of the total pore volume is in pores of diameter between the mode pore diameter and less than about 50, and preferably less than about 25 angstroms below the mode pore diameter.

Generally, the supports and catalysts employed in the process of the invention have steeper-sloped pore size distribution curves than the curves of conventional mild hydrocracking catalysts. As used herein, a steeper slope is a negative slope of greater absolute value than the absolute value of the negative slope of a comparative support or catalyst. The slope, as defined herein, of a pore size distribution curve, derived, for example, from mercury porosimeter testing techniques, [plotting cumulative pore volume (ordinate) vs. pore diameter (logarithmic scale abscissa)], is for a line drawn through a point on the curve representing 40 percent of the total pore volume in pores of diameter above the mode pore diameter and through a point on the curve representing 40 percent of the total pore volume in pores of diameter below the mode pore diameter. More preferably, the support and catalyst used in the process of the invention have steeper slopes than respective conventional supports and catalysts for a line drawn through a point on the curve representing the mode pore diameter and through a point on the curve representing 40 percent of the total pore volume in pores of diameter greater than the mode pore diameter.

Other physical properties of the final mild hydrocracking catalyst typically include a total pore volume of about 0.20 to about 1.0 cc/gram, and preferably about 0.20 to about 0.60 cc/gram and most preferably about 0.25 to about 0.5 cc/gram and a surface area greater than about 100 m²/gram, and preferably between about 100 and 250 m²/gram with both properties determined by the conventional methods previously disclosed herein.

One preferred catalyst employed in the invention contains about 1 to about 6 weight percent of Group VIII metal components, calculated as the monoxide, from about 17 to about 35 weight percent of Group VIB metal components, calculated as the trioxide, and about 1 to about 6 weight percent of phosphorus components, calculated as P, on a porous refractory oxide support consisting essentially of gamma alumina. The most preferred Group VIII and Group VIB metals in this embodiment are cobalt and molybdenum, respectively. Physical characteristics of this catalyst include a total pore volume of about 0.30 to about 0.50 cc/gram, a surface area from about 125 to about 225 m²/gram and a mode pore diameter from about 80 to about 110 angstroms.

A highly preferred catalyst employed in the invention contains about 1 to about 6 weight percent of nickel component, calculated as NiO, from about 17 to about 30 weight percent of molybdenum components, calculated as MoO₃, and about 1 to about 6 weight percent of phosphorus components, calculated as P, on a support containing gamma alumina. This catalyst has a surface area from about 125m²/gram to about 250m²/gram, a mode pore diameter from about 60 to about 90 angstroms, and a pore size distribution wherein at least about 70 percent of the pore volume is in pores of diameter in the range from about 20 angstroms above to about 20 angstroms below the mode pore diameter.

Catalysts are activated in accordance with methods suited to a mild hydrocracking process. Most of the catalysts used in the mild hydrocracking process of the invention are more active, sometimes even far more active, in a sulfided form than in the oxide form in which they are generally prepared. Accordingly, the catalyst used herein may be sulfided prior to use by any known method (in which case the procedure is termed "presulfiding"), for example, by passing a sulfiding agent over the catalyst prepared in the calcined form. Temperatures between 150°C (300°F) and 370°C (700°F) and gaseous space velocities between about 140 and 500 v/v/hr are generally employed, and this treatment is usually continued for at least about two hours. A mixture of hydrogen and one or more components selected from the group consisting of sulfur vapor and sulfur compounds (e.g., lower molecular weight thiols, organic sulfides, and especially H₂S) is suitable for presulfiding. Generally speaking, the relative proportion of sulfiding compounds in the presulfiding mixture is not critical, with any proportion of sulfur ranging between 0.01 and 15 percent by volume, calculated as S, being adequate. Also, liquid sulfiding agents, such as dimethyl disulfide and the like, may be used for presulfiding.

If the catalyst is to be used in a sulfided form, it is preferred that a presulfiding procedure be employed. However, since mild hydrocracking can be employed to upgrade sulfur-containing hydrocarbons (i.e., hydrodesulfurization), one may, as an alternative, accomplish the sulfiding in situ with sulfur-containing hydrocarbon oils, particularly those containing about 1.0 weight percent or more of sulfur, under mild hydrocracking conditions.

The mild hydrocracking catalyst may be employed as either a fixed, slurried or fluidized bed (but most usually a fixed bed) of particulates in a suitable reactor vessel wherein the hydrocarbon oil to be treated is introduced and subjected to mild hydrocracking conditions including an elevated total pressure, temperature, and hydrogen partial pressure. Under such conditions, the hydrocarbon oil and catalyst are subjected to a hydrogen partial pressure usually less than 103 bar (1,500 p.s.i.g.) (frequently less than about 83 bar (1,200 p.s.i.g.) for vacuum gas oil mild hydrocracking) at a space velocity usually less than 3.0 LHSV so as to effect the desired degree of hydrocracking, desulfurization, and denitrogenation. As used herein, "mild hydrocracking" requires the conversion of about 10 to about 50 volume percent of the feedstock hydrocarbons boiling above about 370°C (700°F) to products boiling at or below 370°C (700°F) from a single pass of the feedstock. Preferably, mild hydrocracking conditions are such that at least a 15 volume percent conversion is obtained, and usually no more than a 35 volume percent conversion is obtained.

Contemplated for treatment by the process of the invention are relatively high boiling hydrocarbon-containing oils including crude petroleum oils and synthetic crudes. Among the typical oils contemplated are top crudes, vacuum and atmospheric residual fractions, light and heavy atmospheric and vacuum distillate oils, deasphalted oils, shale oils, and oils from bituminous sands, coal compositions and the like. For use herein, typical hydrocarbon oils, or mixtures thereof, contain at least about 50 volume percent of components normally boiling above about 370°C (700°F) and in some cases, at least 90 volume percent. Also, useful oils may contain up to about 30 volume percent of components boiling above about 565°C (1,050°F).

Generally, a substantial proportion (i.e., at least about 90 volume percent) of hydrocarbon feeds such as gas oils and the like boil at a temperature less than about 595°C (1100°F), preferably less than about 565°C (1050°F), and usually boil entirely within the range of about 38°C (100°F) to about 595°C (1100°F), and most frequently in the range from about 260°C (500°F) to about 595°C (1100°F).

Although virtually any high boiling hydrocarbon feedstock may be treated by mild hydrocracking, the process is particularly suited to treating (1) gas oils, preferably light and heavy vacuum gas oils and waxy shale oils, and (2) heavy residual fractions, especially the treated atmospheric and vacuum residuum oils containing less than about 25 ppmw, and preferably less than 5 ppmw of contaminant metals (vanadium, nickel, and the like). Sulfur is usually present in such oils in a proportion exceeding 0.1 weight percent and often exceeding 1.0 weight percent. Frequently, the feedstock contains undesirable proportions of nitrogen, usually in a concentration greater than about 0.01 weight percent and often between about 0.01 and 1.0 weight percent. The feedstock may contain waxy components, e.g., n-paraffins and slightly-branched paraffins, and thus have a high pour point, e.g., at least about -1°C (30°F).

A hydroprocessing reactor useful in the mild hydrocracking process of the invention is either a newly constructed, existing or modified existing reactor. Ordinarily an existing reactor that is part of an existing hydroprocessing unit, or units, in a refinery is utilized. A preferred reactor is one formerly used for vacuum gas oil desulfurization. In the mild hydrocracking of such a gas oil, the catalyst is usually maintained as a fixed bed with the feedstock passing downwardly once therethrough, and the reactor is generally operated under conditions within the limits of the existing reactor design. In some instances, mild hydrocracking reactors may be added to the existing equipment, either in series or parallel. If the feedstock is unusually high in organonitrogen and organosulfur compounds, it may be pretreated, integrally or separately, using a hydrotreating catalyst.

Typical mild hydrocracking conditions that yield more than about 10 volume percent conversion of the oil fraction boiling above 370°C (700°F) to liquid products boiling at or below 370°C (700°F) are shown in the following Table I:

TABLE I

Operating Conditions	Suitable Range	Preferred Range
Temperature, $^{\circ}\text{C}$	260 - 480	315 - 455
$^{\circ}\text{F}$	500 - 900	600 - 850
Hydrogen Pressure, bar	14 - 103	34 - 90
p.s.i.g.	200 - 1,500	500 - 1,300
Space Velocity, LHSV	0.05 - 3.0	0.1 - 1.5
Hydrogen Recycle Rate, m^3/m^3	89 - 2670	178 - 17,800
scf/bbl	500 - 15,000	1000 - 10,000

Generally, the hydrogen partial pressure maintained during hydrocracking is more than 50 percent of the total pressure. Usually, for once-through operation, the hydrogen partial pressure is between about 85 and 95 percent of the total pressure while, for recycle operation, the hydrogen partial pressure is somewhat lower, i.e., between 80 and 85 percent of the total pressure.

Another preferred reactor utilized in the process of the invention is a hydrodesulfurization reactor formerly used for processing a hydrocarbon residuum feedstock. Ordinarily, this reactor is in the latter stage, or stages, of a multi-stage unit for hydrodesulfurization and/or demetallization of a residuum-containing feedstock. In the case of mild hydrocracking a residuum feedstock, the hydrogen partial pressure is usually higher than that during mild hydrocracking a gas oil. In comparison to conventional hydrodesulfurization conditions that yield, from a single pass, a conversion of less than about 10 volume percent of liquid hydrocarbon products boiling at or below 370°C (700°F), the operating conditions of the process of the invention for mild hydrocracking a residuum hydrocarbon typically include an increased temperature and/or decreased space velocity, correlated to effect a conversion greater than 10 percent.

The mild hydrocracking process of the invention may include either serial or simultaneous desulfurization and denitrogenation of a feedstock. Simultaneous desulfurization, denitrogenation and mild hydrocracking, as used herein, involves contacting a hydrocarbon oil feedstock with the particulate catalyst disclosed herein under conditions effecting (1) a lower sulfur and nitrogen content in the effluent and (2) a

higher percentage of liquid products boiling at or below 370°C (700°F) in the effluent as compared to the feedstock. Serial desulfurization and denitrogenation of a feedstock involves either removing sulfur and nitrogen from the feedstock prior to contact of the mild hydro cracking catalyst disclosed herein or removing sulfur and nitrogen from the effluent of such a mild hydrocracking process.

5 The results obtained in any particular mild hydrocracking process will depend upon the nature of the catalyst, the nature of the feedstock, and the severity of the operating conditions. It is preferred that at least 15 volume percent and, more preferably, at least 20 volume percent of the oil is converted to liquid products boiling at or below 370°C (700°F) in a single pass; however, the maximum conversion is usually less than 50 volume percent and often less than 45 volume percent. It is highly preferred that about 15 to
10 about 35 volume percent of the oil is converted, in a single pass, to liquid products boiling at or below 370°C (700°F), and that at least about 85 volume percent of the 370°C (700°F)-minus fraction contain liquid hydrocarbon products boiling in the midbarrel range from about 150°C (300°F) to about 370°C (700°F).

15 The invention is further illustrated by the following examples which are illustrative of specific modes of practicing the invention and are not intended as limiting the scope of the invention defined by the appended claims.

EXAMPLE I

20 Two catalysts are prepared in accordance with the invention. The first catalyst, Catalyst A, is prepared by extruding a gamma alumina-containing material through a die. The extruded matter, having a cross-sectional shape of a three leaf clover, is broken into particulates and dried at 500°C (930°F). Support particulates, having a nominal 1.3mm (1/20 inch) cross-sectional width (measured by maximum distance
25 across two such clover leaves), are then impregnated with nickel nitrate hexahydrate and ammonium heptamolybdate dissolved in phosphoric acid so as to incorporate into the catalyst, after drying and a calcination, about 4 weight percent nickel components, calculated as NiO, about 25 weight percent molybdenum components, calculated as MoO₃, and about 3 weight percent of phosphorus components, calculated as P.

30 The second catalyst, Catalyst B, is prepared in the same manner as Catalyst A. Catalyst B has the same weight percentages of nickel, molybdenum and phosphorus components as Catalyst A; however a different gamma alumina support is utilized. The porosity characteristics of Catalysts A and B are shown in Table II as follows:

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TABLE II

	<u>Pore Diameter Angstroms</u>	<u>Catalyst A % Pore Volume</u>	<u>Catalyst B % Pore Volume</u>
5	<60	-	5.9%
10	60-65	-	4.9%
	<65	5.7%	-
	65-70	3.2%	4.9%
15	70-80	12.1%	20.6%
	80-90	37.1%	30.3%
20	90-100	32.7%	18.0%
	100-105	2.4%	3.0%
25	>105	6.8%	11.0%
	PORE VOLUME cc/gram (Merc. Poros.)	0.33	0.34
30	MODE PORE DIAMETER (Merc. Poros.)	~87	~83

35 Both catalysts are tested for their activity for mild hydrocracking the hydrocarbon feedstock identified in the following Table III.

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TABLE IIIFeedstock Properties

5	Feed Description	Light Arabian Vacuum Gas Oil
	Gravity, °API	22.3
10	Sulfur, wt. %	2.54
	Nitrogen, wt. %	0.09
	Carbon Residue, D-189, wt. %	0.42
	Pour Point	+35°C (+95°F)
15	ASTM D-1160, Vol. %	Distillation,
	Initial Boiling Point / 5	328/370°C (623/700°F)
	10/20	392/413°C (737/776°F)
20	30/40	432/447°C (810/837°F)
	50/60	460/481°C (860/898°F)
	70/80	498/520°C (928/968°F)
25	90/95	548/569°C (1019/1056°F)
	End Boiling Point / % rec	595°C (1103°F)

The test is conducted by contacting the catalysts in separate runs with the feedstock identified in Table III under mild hydrocracking conditions. However, at the outset of each run, the respective catalysts are presulfided by contact for about 16 to 20 hours with a gas consisting of 90 volume percent H₂ and 10 volume percent H₂S flowing at 125 l/min (4.4 SCFM) (one atmosphere pressure). The temperature during the presulfiding is initially at room temperature, is increased gradually until 370°C (700°F) is reached, and then lowered to 290°C (550°F), at which time the catalyst is contacted with the feedstock.

A portion of the feedstock is passed downwardly through a reactor vessel and contacted in separate runs with Catalysts A, B and a commercial mild hydrocracking catalyst in a single-stage, single-pass system with onecethrough hydrogen. The operating conditions during each run are summarized as follows: 69 bar (1,000 p.s.i.g.) total pressure, 1.0 LHSV, a hydrogen rate of 534m³/m² (3,000 SCF/bbl), and temperature adjusted to determine the conversions obtainable at 377°C (710°F), 391°C (735°F) and 402°C (755°F). The sulfur, nitrogen and mild hydrocracking conversions obtained for each catalyst are set forth in the following Table IV, with it being noted that mild hydrocracking conversion is calculated as the volume percentage of material boiling above 370°C (700°F) converted to material boiling at or below 370°C (700°F).

TABLE IV

	Conversion to 370°C (700°F) - at Temperature			Wt. % Sulfur at Temperature			Wt. % Nitrogen at Temperature		
	°C								
	377	391	402	377	391	402	377	391	402
	°F								
	<u>710</u>	<u>735</u>	<u>755</u>	<u>710</u>	<u>735</u>	<u>755</u>	<u>710</u>	<u>735</u>	<u>755</u>
Commercial Catalyst	18.0	22.6	29.6	—	0.23	0.113	0.040	0.024	0.015
Catalyst A	21.9	31.5	34.2	0.044	0.0056	0.0032	0.005	0.002	0.001
Catalyst B	22.9	30.3	38.0	0.034	0.009	0.005	0.005	0.002	0.001

The data in Table IV clearly indicate that both Catalysts A and B are useful for mild hydrocracking a typical gas oil feedstock. In addition, the data obtained at 391°C (735°F) and 402°C (755°F) evidence the superiority of the processes using Catalysts A and B over that of the commercial catalyst. Based on the data in Table IV, the catalyst of the invention is markedly superior to the commercial catalyst for converting the feed to 370°C (700°F) - products and in its activity for desulfurization and denitrogenation.

Although the invention has been described in conjunction with its preferred embodiment and examples, many variations, modifications, and alternatives will be apparent to those skilled in the art. For example, although the foregoing catalysts were described in relation to their particular usefulness for mild hydrocracking, it is clear from the discoveries in the present invention that such catalysts may also be used for hydrocracking, either alone or in conjunction with conventional small pore hydrocracking catalysts (i.e. catalysts containing zeolitic and/or non-zeolitic molecular sieves having pore sizes having diameters less than about 20 angstroms). Accordingly, it is intended to embrace within the invention all such variations, modifications, and alternatives as fall within the spirit and scope of the appended claims.

Claims

1. A process for simultaneously hydrosulfurizing, hydrodenitrogenating and mild hydrocracking a hydrocarbon feedstock comprising contacting said feedstock containing nitrogen components, sulfur components and feed components boiling above 370°C (700°F) with a particulate catalyst comprising at least one active nickel hydrogenation metal component, at least one active molybdenum hydrogenation metal component and at least one phosphorus component on an amorphous porous refractory oxide, said catalyst having a pore size distribution wherein at least 75 percent of the pore volume is in pores of diameter in the range from about 50 angstroms to about 130 angstroms and less than 10 percent of said pore volume is in pores of diameter greater than 110 angstroms, under conditions such that said sulfur components and said nitrogen components in said feedstock are converted to product components of reduced sulfur and nitrogen content and about 10 to about 50 volume percent of said feed components boiling above 370°C (700°F) are simultaneously converted to product components boiling at or below 370°C (700°F).

2. A process according to claim 1, wherein said conditions include a hydrogen partial pressure less than about 103 bar (1,500 p.s.i.g.).

3. A process according to claim 1 or 2, wherein said catalyst has a mode pore diameter in the range from about 55 to about 100 angstroms.

4. A process according to claim 3, wherein said mode pore diameter is in the range from about 60 to about 90 angstroms.

5. A process according to claim 3 or 4, wherein said catalyst has at least 75 percent of the pore volume in pores of diameter from about 20 angstroms above the mode pore diameter to about 20 angstroms below said mode pore diameter.

6. A process according to any preceding claim, wherein said amorphous porous refractory oxide comprises silica, alumina, silica-alumina, magnesia, silica-magnesia, zirconia, silica-zirconia, titania, silica-titania, or silica-zirconia-titania.

7. A process according to any preceding claim, wherein said conditions yield at least about 20 volume percent conversion of said feed components boiling above 370°C (700°F) to product components boiling at or below 370°C (700°F).

8. A process according to any preceding claim, wherein said catalyst contains up to about 10 weight percent of said nickel hydrogenation metal, calculated as NiO.

9. A process according to claim 8, wherein said catalyst contains from about 17 to about 35 weight percent of said molybdenum components, calculated as MoO₃, and about 2 to about 6 weight percent of said nickel components, calculated as NiO.

10. A process according to any preceding claim, wherein said catalyst contains up to about 30 weight percent of molybdenum hydrogenation metal component, calculated as MoO₃.

11. A process according to any preceding claim, wherein said catalyst contains from 1 to about 6 weight percent of phosphorus components, calculated as P.

12. A process for simultaneously hydrodesulfurizing, hydrodenitrogenating and mild hydrocracking a gas oil or residuum feedstock containing nitrogen components, sulfur components and a substantial proportion of feed components boiling below about 595°C (1100°F) with at least some of said feed components boiling above 370°C (700°F), under conditions of elevated temperature and a hydrogen partial pressure less than about 103 bar (1,500 p.s.i.g.) with a catalyst consisting essentially of from about 2 to about 6 weight percent of at least one nickel metal hydrogenation component, calculated as NiO, and from about 17 to about 27 weight percent of at least one molybdenum metal hydrogenation component, calculated as MoO₃, and from about 1 to about 6 weight percent of at least one phosphorus component, calculated as P, on a support comprising gamma alumina, said catalyst having a pore size distribution wherein the mode pore diameter is in the range from about 60 to about 90 angstroms and at least about 75 percent of the pore volume is in pores of diameter in the range from about 50 angstroms to about 130 angstroms and from about 20 angstroms above the mode pore diameter to about 20 angstroms below said mode pore diameter and less than 10 percent of said pore volume is in pores of diameter greater than 110 angstroms, said conditions being such that said sulfur components and said nitrogen components in said feedstock are converted to product components of reduced sulfur and nitrogen content and between about 10 and 50 percent by volume of said feed components boiling above 370°C (700°F) are simultaneously converted to product components boiling at or less than 370°C (700°F).

13. A process according to claim 12, wherein between about 15 and 35 percent by volume of said feedstock components boiling above 370°C (700°F) are converted to product components boiling at or below 370°C (700°F).

14. A process according to claim 12 or 13, wherein said conditions yield at least about 20 volume percent conversion of the feed components boiling above 370°C (700°F) to product components boiling at or below 370°C (700°F).

15. A process according to claim 12, 13 or 14, wherein said catalyst has at least 80 percent of said pore volume in pores of diameter from about 20 angstroms above the mode pore diameter to about 20 angstroms below said mode pore diameter.

16. A process according to any one of claims 12 to 15, wherein said catalyst has less than 15 percent of said pore volume in pores of diameter greater than 90 angstroms.

17. A process according to any one of claims 12 to 16, wherein said catalyst has less than 10 percent of said pore volume in pores of diameter less than 50 angstroms.



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EUROPEAN SEARCH REPORT

Application number

EP 87 30 3104

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 126 250 (UNION OIL CO.) * Abstract; pages 4-6; page 18, table 1; claims 1-22 *	1-17	B 01 J 27/19 B 01 J 35/10 C 10 G 49/04
Y	--- GB-A-1 357 918 (UNION OIL CO.) * Page 4, lines 10-35; page 5, lines 15-42; page 7, lines 15-43; page 8, lines 5-24; claims 1-29 *	1-17	
A	--- EP-A-0 164 162 (SHELL)		
A	--- FR-A-2 281 788 (CHEVRON)		
D, A	--- US-A-4 028 227 (GUSTAFSON) -----		TECHNICAL FIELDS SEARCHED (Int. Cl.4) B 01 J C 10 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04-08-1987	Examiner LO CONTE C.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document			

